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A Mechanical Model for the Brownian Motion of a Convex Body

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Summary. Under suitable conditions the motion of a massive (Brownian) particle in a fluid is well described by a Langevin equation, i.e. an Ornstein-Uhlenbeck process in which the influence of the fluid on the motion is taken into account by frictional and fluctuating forces. A mechanical model for such a description was previously given for the translational motion of a sphere in an ideal gas in the "Brownian limit". Here that description is extended to include also the rotational motion of a massive convex body. The only probabilistic assumptions concern the initial distribution of the gas; the time evolution of the convex body-ideal gas system is entirely deterministic.

0. Introduction

In [3] we considered the motion of a massive molecule, represented by a sphere of mass M, immersed in an ideal gas of light atoms treated as noninteracting point particles of mass m in the Brownian limit. This limit corresponds to $m \to 0$, while the density of the atoms increases like $m^{-1/2}$ and their (spherically symmetric) velocity distribution is scaled like $f_m(v) = m^{3/2} f(\sqrt{m}v)$. We proved that in this limit the motion of the molecule converges (in distribution) to the Ornstein-Uhlenbeck process (OU process). Here we extend the results of [3] to the case where the molecule has a convex shape and an arbitrary distribution of mass. The motion of the molecule is now one of translation and rotation described respectively by the velocity $\underline{V}_m$ of its center of mass and its angular velocity $\underline{W}_m$. We show that in the Brownian limit the pair $\underline{Z}_m = (\underline{V}_m, \underline{W}_m)$ converges in distribution to $\underline{Z}_0 = (\underline{V}_0, \underline{W}_0)$, a coupled diffusion process with linear drift (friction) coefficient and constant diffusion

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coefficient, a generalized OU process. For technical reasons we restrict ourselves to molecules with smooth surfaces. The restriction to a convex shape however appears essential for the result.

As expected our rigorous derivation leads to the same OU process as that obtained heuristically by making various Markovian assumptions on the interaction of a heavy molecule with light bath particles or other approximations, cf. [2, 4, 6, 8]. The corresponding Fokker-Planck equation for the momentum and angular momentum $\hat{\underline{P}}_0$ and $\hat{\underline{L}}_0$ in a space fixed coordinate system $\hat{\Sigma}$ may be found for special cases in for example [2].

The method used in [3] to establish convergence to the OU process employed a "good coupling" of an abstract Markov process (which converges to the desired OU process) and the true mechanical process: We constructed a simultaneous realization of the Markov process and the mechanical process with the property that the paths of the Markov process were close (in probability) to the paths of the molecule as $m \to 0$. Here we use the same method and construct a good coupling of a Markov process $\tilde{\underline{Z}}_m = (\tilde{\underline{V}}_m, \tilde{\underline{W}}_m)$ which converges to $\underline{Z}_0 = (\underline{V}_0, \underline{W}_0)$, the appropriate generalized OU process, and the mechanical process $\underline{Z}_m$.

The model is described in Sect. 1. In Sect. 2 we state our main theorem and write down the Fokker-Planck equation for the variables $\hat{\underline{P}}_0$, $\hat{\underline{L}}_0$. In Sect. 3 we define the Markov process $\tilde{\underline{Z}}_m$, which converges in distribution to $\underline{Z}_0$. In Sect. 4 we construct a coupling of $\tilde{\underline{Z}}_m$ and $\underline{Z}_m$, and prove that it is a good coupling, thereby establishing the main results.

1. The Mechanical Model

We describe the ideal gas of atoms of mass m (the *bath*) by a Poisson field $(\Omega, \mathscr{F}, P_m)$ built on $(\Gamma, \mathscr{B}(\Gamma), \mu_m)$ [3] where $\Gamma = \mathbb{R}^3 \times \mathbb{R}^3$ denotes the one particle phase space, $\mathscr{B}(\Gamma)$ its Borel algebra and

$$d\mu_m = \lambda_m f_m(v)\, d\underline{q}\, d\underline{v}, \qquad \underline{q}, \underline{v} \in \mathbb{R}^3, \; v = |\underline{v}| \tag{1.1}$$

with

$$\lambda_m = \lambda m^{-1/2}, \qquad \lambda > 0 \tag{1.2}$$

and

$$f_m(v) = m^{3/2} f(\sqrt{m}\, v); \tag{1.3}$$

$f(v)\, d\underline{v}$ is a (spherically symmetric) probability distribution. We assume that the velocity distribution has at least four moments i.e. $\int v^4 f(v)\, d\underline{v} < \infty$.

For a Poisson field the number N_B of particles with coordinates $(\underline{q}, \underline{v})$ in $B \in \mathscr{B}(\Gamma)$ satisfies

$$P_m(\{\omega \in \Omega \mid N_B(\omega) = k\}) = \exp(-\mu_m(B))\, \mu_m(B)^k / k! \tag{1.4}$$

where ω represents a configuration of countably many atoms i.e. $\omega = (\underline{q}_i, \underline{v}_i)_{i \in \mathbb{N}}$. It follows [9] that $\mathscr{F}_A$, the local σ-algebra on $A \subset \Gamma$ (of events depending only upon the configuration in A) is independent of $\mathscr{F}_B$ whenever A and B are disjoint.

Into this bath of atoms we place the molecule (Me), a convex rigid body of mass M with mass distribution which need not be homogeneous. Me has translational as well as rotational degrees of freedom. Let $\hat{\Sigma}$ denote a space fixed coordinate system and Σ the (body fixed, with origin at the center of mass) coordinate system along the principal axes of Me [5]. Let us denote by $\underline{X}(\hat{\underline{X}})$ a vector described in $\Sigma(\hat{\Sigma})$. The orientation of Σ with respect to $\hat{\Sigma}$ may be expressed by a rotation $\theta \in SO(3)$, the three-dimensional rotation group, so that [5]

$$\hat{\underline{X}} = \theta \underline{X}. \tag{1.5}$$

The motion of the molecule may be described in terms of the position $\hat{\underline{Q}}$ and velocity $\hat{\underline{V}}$ of its center of mass, its orientation θ and its angular velocity $\hat{\underline{W}}$. In general the evolution of $\hat{\underline{V}}$ and $\hat{\underline{W}}$ will involve the orientation $\theta(t)$.

The motion may also be described in Σ by $\underline{Q}$, θ, $\underline{V}$ and $\underline{W}$. The isotropy of the bath suggests that in the Browniian limit (cf. Theorem 2.1) the evolution of the pair $\underline{Z} = (\underline{V}, \underline{W})$ will be autonomous, i.e. not involve the orientation θ. We therefore consider mainly the pair $\underline{Z} = (\underline{V}, \underline{W}) \in \mathbb{R}^3 \times \mathbb{R}^3$ instead of the triple $\hat{Z} = (\theta, \hat{\underline{V}}, \hat{\underline{W}}) \in SO(3) \times \mathbb{R}^3 \times \mathbb{R}^3$.

The evolution of the molecule-bath system is determined by free motion together with the interaction (given by elastic collisions) of the molecule with the atoms. The atoms do not interact with each other. We first describe the free motion.

For $\hat{\underline{X}}$ and θ differentiable functions of time [5]

$$\frac{d\hat{\underline{X}}}{dt} = \theta \left(\underline{W} \times \underline{X} + \frac{d\underline{X}}{dt} \right)$$

and for $\frac{d\hat{\underline{X}}}{dt} = 0$

$$\frac{d\underline{X}}{dt} = -\underline{W} \times \underline{X}. \tag{1.6}$$

With $\underline{J} = (J_1, J_2, J_3)$ the angular momentum matrices (the generators of rotations about the coordinate axes) [11]

$$\frac{d\theta}{dt} = (\hat{\underline{W}} \cdot \underline{J})\theta = \theta(\underline{W} \cdot \underline{J}). \tag{1.7}$$

Let $\mathbf{I}$ denote the moment of inertia tensor, which is diagonal in Σ.

$$\hat{\mathbf{I}} = \theta \mathbf{I} \theta^{-1} \tag{1.8}$$

is the moment of inertia tensor in $\hat{\Sigma}$. For the free motion of the molecule and the atoms

$$\frac{d\hat{\underline{v}}}{dt} = 0, \quad \frac{d\hat{\underline{V}}}{dt} = 0, \quad \frac{d\hat{\underline{L}}}{dt} = 0 \tag{1.9}$$

where $\hat{\underline{L}} = \hat{\mathbf{I}} \cdot \hat{\underline{W}}$ is the angular momentum.

Using (1.6) we thus obtain from (1.9)

$$\frac{d\underline{v}}{dt} = -\underline{W} \times \underline{v} \tag{1.10}$$

and

$$\begin{aligned} \frac{d\underline{V}}{dt} &= -\underline{W} \times \underline{V} \\ \frac{d\underline{W}}{dt} &= -\mathbf{I}^{-1} \cdot (\underline{W} \times (\mathbf{I} \cdot W)). \end{aligned} \tag{1.11}$$

Remark. In view of (1.7) and the fact that $\frac{d\hat{\underline{Q}}}{dt} = \hat{\underline{V}} = \theta \underline{V}$, $\hat{\underline{Q}}(t)$ and $\theta(t)$ may be obtained by integration once $\underline{V}(t)$ and $\underline{W}(t)$ are given.

We now describe the interaction through elastic collisions. Let

$$d\underline{\sigma} = -d\sigma\, \underline{n}, \quad |\underline{n}| = 1 \tag{1.12}$$

be an (outward) directed surface element of Me and let $\underline{r}$ be the vector from the center of mass to the surface element $d\sigma$. To describe the elastic collision between Me with velocity $\underline{V}$ and angular velocity $\underline{W}$ and an atom with velocity $\underline{v}$ which takes place in $d\sigma$, we write $\underline{v}_n$ for the normal component

$$\underline{v}_n = \underline{v} \cdot \underline{n}\, \underline{n} \tag{1.13}$$

and $\underline{v}_t$ for the tangential component:

$$\underline{v} = \underline{v}_t + \underline{v}_n \tag{1.14}$$

and similarly

$$\underline{V} = \underline{V}_t + \underline{V}_n. \tag{1.15}$$

Using conservation of momentum, angular momentum and energy we then obtain for the post collision velocities $\underline{V}^+$ and $\underline{v}^+$

$$\underline{v}_t^+ = \underline{v}_t, \quad \underline{V}_t^+ = \underline{V}_t, \tag{1.16}$$

$$\underline{v}_n^+ = -\frac{1-A}{1+A}\underline{v}_n + \frac{2}{A+1}\underline{V}_n^s(\underline{r}), \tag{1.17}$$

$$\underline{V}_n^+ = \underline{V}_n + \frac{2m}{(A+1)M}(\underline{v}_n - \underline{V}_n^s(\underline{r})), \tag{1.18}$$

$$\underline{W}^+ = \underline{W} + \frac{2m}{A+1}((\underline{r} \times \underline{n}) \cdot \mathbf{I}^{-1})((\underline{v}_n - \underline{V}_n^s(\underline{r})) \cdot \underline{n}) \tag{1.19}$$

where

$$A = m(M^{-1} + (\underline{r} \times \underline{n}) \cdot \mathbf{I}^{-1} \cdot (\underline{r} \times \underline{n})) \tag{1.20}$$

and

$$\underline{V}^s(\underline{r}) = \underline{V} + \underline{W} \times \underline{r} \tag{1.21}$$

is the velocity of the surface point $\underline{r}$ of Me. Moreover

$$\underline{V}_n^{s+}(\underline{r}) = \frac{1-A}{1+A}\underline{V}_n^s(\underline{r}) + \frac{2A}{A+1}\underline{v}_n. \tag{1.22}$$

Note that

$$\begin{aligned} \delta\underline{V} &= \underline{V}^+ - \underline{V} = \frac{2m}{M(A+1)}(\underline{v}_n - \underline{V}_n^s(\underline{r})) \\ \delta\underline{W} &= \underline{W}^+ - \underline{W} = \frac{2m}{A+1}((\underline{r}\times\underline{n})\cdot\mathbf{I}^{-1})((\underline{v}_n - \underline{V}_n^s(\underline{r}))\cdot\underline{n}). \end{aligned} \tag{1.23}$$

The mechanical process $\underline{Z}_{m,t} = (\underline{V}_{m,t}, \underline{W}_{m,t})$, $t\in\mathbb{R}$ is defined as follows: At time $t=0$ we place Me into the bath with configuration $\omega\in\Omega$, at $\underline{Q}^0$ with orientation θ^0 and "velocity" $\underline{Z}_{m0} = \underline{Z}^0 = (\underline{V}^0, \underline{W}^0)$. (We remove from ω all atoms inside the region occupied by Me). Let τ_1 be the time of the first collision of the molecule with an atom of ω, i.e. up to time τ_1 Me undergoes free motion, given by (1.11). $\underline{V}_{m,\tau_1^-}$, $\underline{W}_{m,\tau_1^-}$ change according to (1.18), (1.19) to $\underline{V}^1 = \underline{V}_{m,\tau_1}$, $\underline{W}^1 = \underline{W}_{m,\tau_1}$ and Me undergoes free motion (1.11) with the new initial data $\underline{V}^1$, $\underline{W}^1$ until the next collision at $\tau_2(\omega)$, etc. Each colliding atom changes its velocity according to (1.17) and then moves freely until it collides again with the molecule.

We shall call a collision tangential if $\underline{V}_n^s(\underline{r}) = \underline{v}_n$. Since the molecule can rotate, the time evolution after a tangential collision might not be determined by the laws for elastic collisions. In the same way an infinite number of collisions in a finite amount of time or multiple collisions are problematical. It is only for those configurations $\omega\in\Omega$ and initial data of the molecule for which the molecule suffers only finitely many collisions in a finite amount of time and which do not lead to tangential or multiple collisions that the motion of the molecule is well defined. In the Appendix we show that the motion is well defined for ($P_m \times$ Lebesgue measure) almost every ω and initial data for the molecule, i.e. for almost every $\underline{Z}^0$ the mechanical process is well defined.

Thus, we obtain $\underline{Z}_{m,\cdot} = \mathbf{Z}_m(\underline{Z}_m(t,\omega) = \underline{Z}_{m,t}(\omega))$ as a right continuous process on Ω. For any finite time interval $J\subset\mathbb{R}^+$ let $D(J)$ denote the space of right continuous functions $\underline{y}$: $J\to\mathbb{R}^3\times\mathbb{R}^3$, equipped with the Skorohod topology [8]. We may represent $\underline{Z}_m$ on $(D(J), \mathscr{B}(D(J)), \nu_m)$, where ν_m denotes the measure induced by $\underline{Z}_m$ on $\mathscr{B}(D(J))$, the Borel algebra on $D(J)$.

2. The Result

We use the following notation for the tensors describing the surface of the molecule. We consider only molecules whose surfaces are smooth (or more generally of bounded mean curvature).

$$\mathbf{N} = \int d\sigma\, \underline{n}\underline{n}, \tag{2.1}$$

$$\mathbf{T} = \int d\sigma\, \underline{r}\times\underline{n}\underline{n}, \tag{2.2}$$

$$\mathbf{K} = \int d\sigma\, \underline{r}\times\underline{n}\underline{r}\times\underline{n} \tag{2.3}$$

where $\underline{n}\underline{n}$ = tensor product.

Furthermore we introduce the symmetric positive semidefinite 6×6 matrix ("*" = transpose)

$$\mathscr{D}=\int d\sigma\, \underline{e}_n\underline{e}_n=\begin{pmatrix}\mathbf{N} & \mathbf{T}^*\\ \mathbf{T} & \mathbf{K}\end{pmatrix},\qquad \underline{e}_n=\begin{pmatrix}\underline{n}\\ \underline{r}\times\underline{n}\end{pmatrix} \tag{2.4}$$

and we denote by $\mathscr{D}^{\frac{1}{2}}$ its symmetric positive semidefinite square root.

Let

$$\mathscr{M}^{-1}=\begin{pmatrix}M^{-1} & 0\\ 0 & \mathbf{I}^{-1}\end{pmatrix};\qquad \mathbf{1}=3\times 3 \text{ unit matrix} \tag{2.5}$$

and

$$\phi_i=\tfrac{1}{2}\int |v_x|^i f(v)\,d\underline{v}\qquad i=1,\ldots,4,\ \underline{v}=(v_x,v_y,v_z). \tag{2.6}$$

Theorem 2.1. *Let $\underline{Z}_0=(\underline{V}_0,\underline{W}_0)$ denote the (generalized) Ornstein-Uhlenbeck-process given by the stochastic differential equation*

$$d\underline{Z}_{0,t}=-\begin{pmatrix}\underline{W}_{0,t}\times\underline{V}_{0,t}\\ \mathbf{I}^{-1}\cdot(\underline{W}_{0,t}\times\mathbf{I}\cdot\underline{W}_{0,t})\end{pmatrix}dt-4\lambda\phi_1\mathscr{M}^{-1}\mathscr{D}\cdot\underline{Z}_{0,t}\,dt$$
$$+\sqrt{4\lambda\phi}_3\mathscr{M}^{-1}\mathscr{D}^{1/2}\cdot d\underline{B}_t, \tag{2.7}$$

where $\underline{B}_t$ is the 6-dimensional standard Wiener process. Suppose that $\underline{Z}_{m,0}$, $m>0$, and $\underline{Z}_{0,0}$ have the same absolutely continuous distribution $\rho(d\underline{Z})$. Then $\underline{Z}_m$ converges in distribution to $\underline{Z}_0$ as $m\to 0$. ($\underline{Z}_m \overset{\mathscr{D}}{\Rightarrow} \underline{Z}_0$). □

Remarks. (i) $\underline{Z}_m \overset{\mathscr{D}}{\Rightarrow} \underline{Z}_0$ is equivalent to the statement that for any J the measures ν_m on $D(J)$ induced by $\underline{Z}_m$ converge weakly to ν_0, the measure induced by $\underline{Z}_0$, as $m\to 0$ [1].

(ii) It is easily checked that the stationary distribution of $\underline{Z}_0$ is the Maxwellian

$$P_{st}(\underline{Z})\propto\exp(-\tfrac{1}{2}\beta(M\underline{V}^2+\underline{W}\cdot\mathbf{I}\cdot\underline{W})),\qquad \beta=2\phi_1/\phi_3.$$

(iii) From Theorem 2.1 it follows that on $\hat{D}(J)$, the space of right continuous functions $\hat{\underline{y}}\colon J\to SO(3)\times\mathbb{R}^3\times\mathbb{R}^3$,

$$\hat{\underline{Z}}_m=(\theta_m,\hat{\underline{V}}_m,\hat{\underline{W}}_m)\overset{\mathscr{D}}{\Rightarrow}\hat{\underline{Z}}_0=(\theta_0,\theta_0\underline{V}_0,\theta_0\underline{W}_0), \tag{2.8}$$

since the mapping

$$\Psi(\underline{V}_m,\underline{W}_m)=(\theta_m,\theta_m\underline{V}_m,\theta_m\underline{W}_m)$$

is continuous [1].

It is now a routine matter of stochastic calculus [10] to write down the Fokker-Planck equation for the transition probability density of the process $(\theta_0,M\hat{\underline{V}}_0,\hat{\mathbf{I}}\hat{\underline{W}}_0)=(\theta_0,\hat{\underline{P}}_0,\hat{\underline{L}}_0)$, $\rho(\theta,\hat{\underline{P}},\hat{\underline{L}},t|\theta^0,\hat{\underline{P}}^0,\hat{\underline{L}}^0)$:

$$\frac{\partial\rho}{\partial t}=-\frac{\partial}{\partial\theta}(\hat{\mathbf{I}}^{-1}\hat{\underline{L}})\cdot\underline{J}\,\theta\rho+\left[4\lambda\phi_1\left\{\frac{\partial}{\partial\hat{\underline{P}}}\cdot(\hat{\mathbf{N}}\cdot\hat{\underline{P}}M^{-1}+\hat{\mathbf{T}}^*\hat{\mathbf{I}}^{-1}\cdot\hat{\underline{L}})\right.\right.$$
$$\left.+\frac{\partial}{\partial\hat{\underline{L}}}\cdot(\hat{\mathbf{T}}\hat{\underline{P}}M^{-1}+\hat{\mathbf{K}}\hat{\mathbf{I}}^{-1}\cdot\hat{\underline{L}})\right\}$$
$$\left.+2\lambda\phi_3\left(\frac{\partial}{\partial\hat{\underline{P}}}\cdot\hat{\mathbf{N}}\cdot\frac{\partial}{\partial\hat{\underline{P}}}+2\frac{\partial}{\partial\hat{\underline{L}}}\cdot\hat{\mathbf{T}}\cdot\frac{\partial}{\partial\hat{\underline{P}}}+\frac{\partial}{\partial\hat{\underline{L}}}\cdot\hat{\mathbf{K}}\cdot\frac{\partial}{\partial\hat{\underline{L}}}\right)\right]\rho. \tag{2.9}$$

Here $\frac{\partial}{\partial\theta}C=\sum_{i,j}\frac{\partial}{\partial\theta_{ij}}C_{ij}$. $\hat{\mathbf{N}},\ldots$ denote the matrices $\mathbf{N},\ldots$ described in $\hat{\Sigma}$ (cf. (1.9)). The Fokker-Planck equation (2.9) has been given for example in [2]. Setting $M=\infty$, but keeping $\mathbf{I}$ finite in (2.7) describes the situation in which the molecule is fixed at one body point about which it may rotate freely. The corresponding *FP* equation for $\rho(\theta,\hat{\underline{L}},t|\theta^0,\hat{\underline{L}}^0)$ may be obtained from (2.9) by omitting all terms involving $\hat{\underline{P}}$. This rotational Brownian Motion has been considered for example in [4, 6, 8].

The proof of Theorem 2.1 is similar to the proof of Theorem 2.1 in [3]. We begin by constructing in the next section a family of abstract Markov processes $\tilde{\underline{Z}}_m$ for which we establish $\tilde{\underline{Z}}_m \overset{\mathcal{S}}{\Rightarrow} \underline{Z}_0$.

3. The Markov Approximation

Lemma 3.1. *Suppose that at time t the molecule has coordinates* $(\hat{\underline{Q}},\theta,\underline{V},\underline{W})$ *and is surrounded by a bath of atoms having the Poisson distribution described in* (1.1)-(1.4). *The probability* $p_m(dt,d\underline{v},d\underline{\sigma},\underline{Z})$ *for the collision with the molecule of an atom with velocity* $\underline{v}\in d\underline{v}$ *in a surface element* $d\underline{\sigma}$ *during the time interval* $[t,t+dt]$ *is given by*

$$p_m(dt,d\underline{\sigma},d\underline{v},\underline{Z})=\lambda_m\,d\sigma(v_n-V_n^s(\underline{r}))_+\,dt\,f_m(v)\,d\underline{v} \tag{3.1}$$

where $(v_n-V_n^s(\underline{r}))_+=\max(v_n-V_n^s(\underline{r}),0)$ *and*

$$v_n=\underline{v}_n\cdot\underline{n},\qquad V_n^s(\underline{r})=\underline{V}_n^s(\underline{r})\cdot\underline{n}.\quad\square \tag{3.2}$$

Proof. For the occurrence of the collision, an atom with velocity $\underline{v}\in d\underline{v}$ has to be in a volume element $d\sigma(v_n-V_n^s(\underline{r}))_+\,dt\,d\underline{v}$, whose measure in view of (1.4) is given by (3.1). $\square$

Setting

$$N_m(\underline{Z})=\int d\sigma\int(v_n-V_n^s(r))_+\,f_m(v)\,d\underline{v} \tag{3.3}$$

we obtain a "collision" probability

$$g_m(\underline{r},\underline{v},\underline{Z})\,d\underline{v}\,d\sigma=N_m(\underline{Z})^{-1}(v_n-V_n^s(\underline{r}))_+\,f_m(v)\,d\underline{v}\,d\sigma. \tag{3.4}$$

Let

$$\underline{V}_{m,t}^s(\underline{r})=\underline{V}_{m,t}+\underline{W}_{m,t}\times\underline{r} \tag{3.5}$$

and let S denote the surface of the molecule. We introduce

$$\zeta_{m,t}=\sup_{\underline{r}\in S}|\underline{V}_{m,t}^s(\underline{r})|. \tag{3.6}$$

Let c_m be an increasing function of m^{-1} with $c_m\to\infty$ as $m\to 0$. With

$$\bar{\lambda}_m=\bar{\lambda}_m(\underline{Z})=\lambda_m\min[N_m(\underline{Z}),\sup_{\zeta\le c_m}N_m(\underline{Z})] \tag{3.7}$$

we define a modified "collision" probability

$$p_m(dt,d\underline{\sigma},d\underline{v},\underline{Z})=\bar{\lambda}_m g_m(\underline{r},\underline{v},\underline{Z})\,d\underline{v}\,dt\,d\sigma, \tag{3.8}$$

Definition 3.1. Let $\tilde{\underline{Z}}_m$ be the flow-jump Markov process on the probability space $(\tilde{\Omega}, \tilde{\mathscr{F}}, \tilde{P}_m)$ defined by the flow given by the free motion (1.11) and jumps, determined by the collision Eqs. (1.16)–(1.19), which occur with frequency given by the "collision" rates

$$R_m(\underline{r}, \underline{v}, \underline{Z}) = \bar{\lambda}_m g_m(\underline{r}, \underline{v}, \underline{Z}), \tag{3.9}$$

i.e. $\underline{Z}$ changes in a collision according to (1.16)–(1.19), and in between two collisions according to the free motion described in (1.11). □

Theorem 3.1. *Suppose* $\tilde{Z}_{m,0}$, $m>0$, *and* $\underline{Z}_{0,0}$ *have the distribution* $\rho(d\underline{Z})$. *Then* $\tilde{\underline{Z}}_m \overset{\mathscr{D}}{\Rightarrow} \underline{Z}_0$. □

Proof. Just as in [3] it suffices to establish the strong convergence of the generator [7] $\tilde{A}^{(m)}$ of $\tilde{\underline{Z}}_m$ to the generator A of $\underline{Z}_0$ in sup-norm $\|\cdot\|$:

$$\lim_{m \to 0} \|\tilde{A}^{(m)} h - A h\| = 0 \tag{3.10}$$

for $h \in C_c^\infty$, a core for A. (C_c^∞ is the set of infinitely differentiable functions of compact support on $\mathbb{R}^6$). The restriction of A to C_c^∞ (again denoted by A) may be easily deduced from (2.7) [10]:

$$A = -\begin{pmatrix} \underline{W} \times \underline{V} \\ \mathbf{I}^{-1}(\underline{W} \times \mathbf{I} \cdot \underline{W}) \end{pmatrix} \cdot \nabla - 4\lambda\phi_1 \underline{Z} \cdot \mathscr{D}\mathscr{M}^{-1} \cdot \nabla + 2\lambda\phi_3 \nabla \cdot \mathscr{M}^{-1} \mathscr{D} \mathscr{M}^{-1} \cdot \nabla, \tag{3.11}$$

where

$$\nabla = \frac{\partial}{\partial \underline{Z}} = \left(\frac{\partial}{\partial \underline{V}}, \frac{\partial}{\partial \underline{W}} \right).$$

Let us denote by $\underline{\delta}(\underline{r}, \underline{v})$ the change in $\underline{Z}$ due to a collision with an atom with velocity $\underline{v}$ at $\underline{r} \in S$ as given by (1.23). Then

$$\begin{aligned} (\tilde{A}^{(m)} h)(\underline{Z}^0) = &-\begin{pmatrix} \underline{W} \times \underline{V} \\ \mathbf{I}^{-1}(\underline{W} \times \mathbf{I} \cdot \underline{W}) \end{pmatrix} \cdot \nabla h(\underline{Z}^0) \\ &+ \bar{\lambda}_m(\underline{Z}^0) \{ -h(\underline{Z}^0) + \iint d\sigma\, g_m(\underline{r}, \underline{v}, \underline{Z}^0)\, h(\underline{Z}^0 + \underline{\delta}(\underline{r}, \underline{v}))\, d\underline{v} \}, \end{aligned} \tag{3.12}$$

on C_c^∞. Let $\underline{Z}(\underline{Z}^0, t)$ denote the solution of the equations of free motion, (1.11). (3.12) follows from the observation that for the expectation $\tilde{E}_{\underline{Z}^0}^{(m)}(\cdot)$ corresponding to the process $\tilde{\underline{Z}}_m$ starting at $\underline{Z}^0$,

$$\begin{aligned} \tilde{E}_{\underline{Z}^0}^{(m)}(h(\tilde{\underline{Z}}_{m,t})) = &\exp\left\{ -\int_0^t dt'\, \bar{\lambda}_m(\underline{Z}(\underline{Z}^0, t')) \right\} h(\underline{Z}(\underline{Z}^0, t)) \\ &+ \int_0^t dt' \exp\left\{ -\int_0^{t'} \bar{\lambda}_m(\underline{Z}(\underline{Z}^0, t''))\, dt'' \right\} \\ &\cdot \bar{\lambda}_m(\underline{Z}(\underline{Z}^0, t')) \iint d\sigma\, d\underline{v}\, g_m(\underline{r}, \underline{v}, \underline{Z}(\underline{Z}^0, t')) \\ &\cdot \exp\left\{ -\int_{t'}^t dt''\, \bar{\lambda}_m(\underline{Z}(\underline{Z}(\underline{Z}^0, t') + \underline{\delta}(\underline{r}, \underline{v}), t'' - t')) \right\} \\ &\cdot h(\underline{Z}(\underline{Z}(\underline{Z}^0, t') + \underline{\delta}(\underline{v}, \underline{r}), t - t')) + O(t^2) \end{aligned}$$

$$= \left\{1 - \int_0^t dt' \, \bar{\lambda}_m(\underline{Z}(\underline{Z}^0, t'))\right\} h(\underline{Z}(\underline{Z}^0, t))$$
$$+ \int_0^t dt' \, \bar{\lambda}_m(\underline{Z}(\underline{Z}^0, t')) \iint d\sigma \, d\underline{v} \, g_m(\underline{r}, \underline{v}, \underline{Z}(\underline{Z}^0, t'))$$
$$\cdot \, h(\underline{Z}(\underline{Z}(\underline{Z}^0, t') + \delta(\underline{r}, \underline{v}), t - t')) + O(t^2)$$

since $\bar{\lambda}_m$ is bounded.

To establish (3.10) is now a routine computation. Using

$$\underline{V}_n^s(\underline{r}) = \underline{Z} \cdot \underline{e}_n, \tag{3.13}$$

$$\Delta \underline{Z} = \underline{\delta}(\underline{r}, \underline{v}) = \frac{2m}{A+1}(v_n - V_n^s(\underline{r}))\underline{e}_n \cdot \mathscr{M}^{-1} \tag{3.14}$$

and (2.4), the computations are essentially the same as in Sect. 4 of [3] and are left to the reader.

4. The Coupling

In order to simplify the equations of this section we set $M=1$, $\lambda=1$ and we normalize the surface, $\int d\sigma = 1$. Furthermore we fix $J=[0, T]$, $T<\infty$.

Definition 4.1. Let $\underline{X}_{m,t}$, $\underline{Y}_{m,t}$, $t \in J$ have the same state space, equipped with a norm $|\cdot|$. A *good coupling* of $\underline{X}_m$ and $\underline{Y}_m$ is a joint realization $\underline{X}'_m$ of $\underline{X}_m$ and $\underline{Y}'_m$ of Y_m, on a probability space $(\bar{\Omega}, \bar{\mathscr{F}}, \bar{P}_m)$, such that for all $\varepsilon > 0$

$$\lim_{m \to 0} \bar{P}_m(\{\bar{\omega} \in \bar{\Omega} | \sup_{t \in J} |\underline{X}'_m(t, \bar{\omega}) - \underline{Y}'_m(t, \bar{\omega})| > \varepsilon\}) = 0. \quad \square \tag{4.1}$$

Theorem 2.1 follows [1] from the following

Theorem 4.1. *There exists a good coupling of $\tilde{\underline{Z}}_m$ and $\underline{Z}_m$.* $\square$

Proof. We first construct for each $k>0$ a coupling $(\tilde{\underline{Z}}'_m, \underline{Z}'_m)$; we later prove that from this family of couplings a good coupling can be extracted. (We suppress the dependence of $\tilde{\underline{Z}}'_m$ and $\underline{Z}'_m$ on k.)

We will call an atom in a collision "slow" if its precollision velocity $\underline{v}$ satisfies $|\underline{v}_n| < k$, and "fast" if $|\underline{v}_n| \geqq k$. From now on we assume m so small that $c_m > k$ (c.f. Eq. (3.7)).

Remark 4.1. In establishing Theorem 4.1 we shall use the fact that the surface of the molecule is convex. This insures that in the mechanical process $\underline{Z}_m$ until $\zeta_{m,t} \geqq k$ ((3.6)) no "fast" atom could have collided earlier. (This may be seen by tracing the paths of the atom and the molecule from the collision on backwards in time. Note that the atom is then moving away from the tangent plane through the collision point on the surface of Me with a speed $\geqq k$). Hence, by the "strong Markov property" for the Poisson field [10], until $\zeta_{m,t} \geqq k$ the fast atoms with which the molecule collides are all "Poisson distributed", so that the collisions between Me and fast atoms are governed by the rates (3.9). (Note that $\bar{\lambda}_m = m^{-1/2} N_m(\underline{Z})$ for $\zeta \leqq k < c_m$.)

We denote by Ma the "Markov molecule" whose motion defines the realization $\tilde{\underline{Z}}'_m$ of the Markov process $\tilde{Z}_m$. We use $\underline{Z}(\tilde{\underline{Z}}')$ as the generic variable for Me(Ma). Me and Ma have the same initial conditions. Given a configuration $\omega\in\Omega$ and thus the motion $\underline{Z}_{m,t}(\omega)$ of Me, we specify the corresponding motion of Ma in two steps:

(i) We observe the motion of Me. When, and only when, Me undergoes a collision with a fast atom (fast collision), with velocity $\underline{v}$ at $\underline{r}$, Ma also "undergoes a collision" with the same $\underline{v}, \underline{r}$, i.e. it changes its velocity and angular velocity according to (1.16), (1.18) and (1.19). Ma also "suffers collisions" from slow atoms according to the rates $R_m(\underline{r}, \underline{v}, \tilde{\underline{Z}}')$, $|\underline{v}_n|<k$. (Between collisions Me undergoes free motion.)

Let $\tau=\inf\{t\geqq 0|\zeta_{m,t}\geqq k\}$. Note that after time τ collisions with Me by fast atoms are no longer governed by the rates R_m and that even for $t<\tau$, it is not in general true that $R_m(\underline{r}, \underline{v}, \underline{Z})=R_m(\underline{r}, \underline{v}, \tilde{\underline{Z}}')$, since slow atoms will cause $\underline{Z}$ and $\tilde{\underline{Z}}'$ to differ.

(ii) To obtain a process with the correct rates $R_m(\underline{r}, \underline{v}, \tilde{\underline{Z}}')$ we modify (i) by either ignoring some fast collisions (so that they produce no effect on Ma) or adding some fast "extra collisions", depending on whether $R_m(\underline{r}, \underline{v}, \tilde{\underline{Z}}')$ is less than or greater than $R_m(\underline{r}, \underline{v}, \underline{Z})$, $|\underline{v}_n|\geqq k$.

a) The probability that a fast collision of (i) counts is

$$P_m(\underline{r}, \underline{v}, \tilde{\underline{Z}}', \underline{Z})=\min\left(\frac{R_m(r, \underline{v}, \tilde{\underline{Z}}')}{R_m(\underline{r}, \underline{v}, \underline{Z})}, 1\right) \quad \text{for } t<\tau \tag{4.2}$$

and is 0 for $t\geqq\tau$.

b) The rate for the occurrence of these extra collisions is ($v_n\geqq k$)

$$R_m(\underline{r}, \underline{v}, \tilde{\underline{Z}}', \underline{Z})=\max(R_m(\underline{r}, \underline{v}, \tilde{\underline{Z}}')-R_m(\underline{r}, \underline{v}, \underline{Z}), 0) \tag{4.3}$$

for $t<\tau$ and is $R_m(\underline{r}, \underline{v}, \tilde{\underline{Z}}')$ for $t\geqq\tau$.

Thus we obtain a Markov process $\tilde{\underline{Z}}'_m$ which is a realization of $\tilde{\underline{Z}}_m$. Let $(\bar{\Omega}, \bar{\mathscr{F}}, \bar{P}_m)$ be a probability space on which the coupling $(\underline{Z}'_m, \tilde{\underline{Z}}'_m)$ of $\underline{Z}_m$ and $\tilde{\underline{Z}}_m$ is realized. (We may take $\bar{\Omega}$ to be a product space $\bar{\Omega}=\Omega\times H$, where H governs the purely stochastic effects, i.e. ignored collisions and extra collisions. A realization $\underline{Z}'_m$ of $\underline{Z}_m$ is defined on $\bar{\Omega}$ in the obvious way: $\underline{Z}'_m(\bar{\omega})=\underline{Z}'_m(\omega, h)=\underline{Z}_m(\omega)$, for $\bar{\omega}=(\omega, h)\in\bar{\Omega}$. To simplify the notation we write $\underline{Z}_m$ instead of $\underline{Z}'_m$.)

For $n>0$ we set ($|\cdot|=$Euclidean norm on $\mathbb{R}^6$)

$$G_n=\{\underline{x}\in D(J)|\sup_{t\in J}|\underline{x}(t)|<n\}. \tag{4.4}$$

Let $\tilde{\nu}_m$ denote the measure induced by $\tilde{Z}'_m$ (or $\tilde{Z}_m$) on $D(J)$, i.e. for $B\in\mathscr{B}(D(J))$, $\bar{P}_m(\{\bar{\omega}\in\bar{\Omega}|\tilde{\underline{Z}}'_m(\omega)\in B\})=\tilde{\nu}_m(B)$. Theorem 3.1 implies [1] that

$$\limsup_{m\to 0}\tilde{\nu}_m(\bar{G}_n)\leqq\nu_0(\bar{G}_n), \tag{4.5}$$

where $\bar{G}_n$ denotes the complement of G_n, and ν_0 the measure induced by $\underline{Z}_0$. Let

$$G_n^m=\{\bar{\omega}\in\bar{\Omega}|\sup_{t\in J}|\tilde{\underline{Z}}'_{m,t}(\omega)|<n\}. \tag{4.6}$$

Lemma 4.1. *For any $n>0$ and $t_0>0$ there exists a $k=k(n)$ such that if*

$$\lim_{m\to 0} \bar{P}_m(G_n^m \cap \{\sup_{0\leqq t\leqq t_0} |\tilde{\underline{Z}}'_{m,t} - \underline{Z}_{m,t}| \geqq \varepsilon\}) = 0 \tag{4.7}$$

for all $\varepsilon>0$, then

$$\lim_{m\to 0} \bar{P}_m(G_n^m \cap \{\sup_{0\leqq t\leqq t_0+u} |\tilde{\underline{Z}}'_{m,t} - \underline{Z}_{m,t}| \geqq \varepsilon\}) = 0 \tag{4.8}$$

for all $\varepsilon>0$, where

$$u = \min[(16n(1+I_0^{-1}I^0))^{-1}, (40\phi_1(1+r_0)(1+r_0 I_0^{-1}))^{-1}, T-t_0],$$

$I^0(I_0)$ is the maximum (minimum) of the principal moments of inertia of Me, and $r_0 = \max_{\underline{r}\in S} |\underline{r}|$. □

(Here $(\tilde{\underline{Z}}'_m, \underline{Z}_m)$ is the coupling constructed using k.)

Remark. Theorem 4.1 follows from Lemma 4.1: Since $\tilde{\underline{Z}}'_m(0) = \underline{Z}_m(0)$, the hypothesis (4.7) of Lemma 4.1 is fulfilled for $t_0=0$, and we obtain that for all $\varepsilon>0$

$$\lim_{m\to 0} \bar{P}_m(G_n^m \cap \{\sup_{0\leqq t\leqq t_0+u} |\tilde{\underline{Z}}'_{m,t} - \underline{Z}_{m,t}| \geqq \varepsilon\}) = 0.$$

Applying Lemma 4.1 repeatedly until T is surpassed yields

$$\lim_{m\to 0} \bar{P}_m(G_n^m \cap \{\sup_{0\leqq t\leqq T} |\tilde{\underline{Z}}'_{m,t} - \underline{Z}_{m,t}| \geqq \varepsilon\}) = 0.$$

But

$$\begin{aligned} &\limsup_{m\to 0} \bar{P}_m(\{\sup_{0\leqq t\leqq T} |\tilde{\underline{Z}}'_{m,t} - \underline{Z}_{m,t}| \geqq \varepsilon\}) \\ &\quad \leqq \limsup_{m\to 0} \bar{P}_m(G_n^m \cap (\{\sup_{0\leqq t\leqq T} |\tilde{\underline{Z}}'_{m,t} - \underline{Z}_{m,t}| \geqq \varepsilon\}) \\ &\quad + \limsup_{m\to 0} \bar{P}_m(\bar{G}_n^m) = \limsup_{m\to 0} \tilde{\nu}_m(\bar{G}_n) \leqq \nu_0(\bar{G}_n) \end{aligned} \tag{4.9}$$

by (4.5). Since

$$\lim_{n\to\infty} \nu_0(\bar{G}_n) = 0 \tag{4.10}$$

it follows easily from (4.9) that we obtain a good coupling by allowing k to vary appropriately with m.

(4.10) states that an explosion (i.e. the process runs out to infinity in finite time) of the (generalized) OU process is impossible. Since the free motion part of the drift in (2.7) is not Lipschitz the usual theorems for the global existence of a solution of a stochastic differential equation cannot be used directly to establish (4.10). But a simple transformation of variables $\underline{Z}_0 \to (\theta_0, \theta_0 \underline{V}_0, \theta_0 \mathbf{I}\cdot \underline{W}_0) = (\theta_0, \hat{\underline{P}}_0, \hat{\underline{L}}_0)$ (using for example the Ito-formula) yields stochastic differential equations with Lipschitz coefficients for $d\hat{\underline{P}}_0$ and $d\hat{\underline{L}}_0$; in (2.9) we have given the corresponding F.P.E. Thus the global existence and uniqueness of the solution of (2.7) follows from the global existence and uniqueness of the process $(\theta_0, \hat{P}_0, \hat{L}_0)$. It is also possible to establish (4.10) directly by applying an explosion test to (2.7) [10].

Proof of Lemma 4.1. Fix n, $\varepsilon>0$ and t_0 and introduce the stopping time

$$t_m^* = \inf_{t \geqq 0} \{t \mid |\tilde{\underline{Z}}'_{m,t} - \underline{Z}_{m,t}| \geqq \varepsilon\}. \tag{4.11}$$

Since $\tilde{\underline{Z}}'_{m,t}$ and $\underline{Z}_{m,t}$ are right continuous $|\tilde{\underline{Z}}'_{m,t_m^*} - \underline{Z}_{m,t_m^*}| \geqq \varepsilon$. Observe that

$$\begin{aligned}\{\sup_{0 \leqq t \leqq t_0+u} |\tilde{\underline{Z}}'_{m,t} - \underline{Z}_{m,t}| \geqq \varepsilon\} &= \{t_m^* \leqq t_0+u\} \\ &= \{t_m^* \leqq t_0+u, |\tilde{\underline{Z}}'_{m,t_m^*} - \underline{Z}_{m,t_m^*}| \geqq \varepsilon\}\end{aligned}$$

and that

$$|\tilde{\underline{Z}}'_{m,s} - \underline{Z}_{m,s}| < \varepsilon, \quad s < t_m^*. \tag{4.12}$$

We choose $k = k(n) \geqq 8n(1+r_0)$. Then on G_n^m, $\tilde{\zeta}'_m < k/8$. By virtue of (4.12) we obtain that on G_n^m for $\varepsilon < n$

$$\sup_{t<t_m^*} |\underline{Z}_{m,t}| < 2n; \quad \sup_{t<t_m^*} \zeta_{m,t} < k/4. \tag{4.13}$$

We have using (1.17) and (4.13) that on G_n^m during $[0, t_m^*]$ a fast atom ($|\underline{v}_n| \geqq k$) which collides with Me bounces off with $|\underline{v}_n^+| > k/4$ for m small enough ($A < 1/10$), and therefore cannot recollide with the molecule during this interval.

Remark 4.2. From this observation and Remark 4.1 it follows that on G_n^m during $[0, t_m^*]$ the only atoms with which Me can recollide are slow atoms, both for the original collisions and for recollisions.

Thus for $\bar{\omega} \in \bar{\Omega}$ we have for $t_m^* > t_0$

$$\begin{aligned}|\tilde{\underline{Z}}'_m(t_m^*) - \underline{Z}_m(t_m^*)| = |&\sum_{i \in B} (\underline{X}'_m(i) - \underline{X}_m(i)) + \underline{Y}'(t_m^*) - \underline{Y}_m(t_m^*) \\ &+ \sum_{i \in E'} \underline{X}'_m(i) - \sum_{i \in E} \underline{X}_m(i) + \underline{F}'_m(t_m^*) - \underline{F}_m(t_m^*) + \tilde{\underline{Z}}'_m(t_0) - \underline{Z}_m(t_0)|,\end{aligned} \tag{4.14}$$

where $\underline{Y}_m(t)(\underline{Y}'_m(t))$ denotes the change in $\underline{Z}_m(\tilde{\underline{Z}}'_m)$ during the time interval $[t_0, t]$ produced by collisions with slow atoms; $\underline{X}_m(i)(\underline{X}'_m(i))$ denotes the change in $\underline{Z}_m(\tilde{\underline{Z}}'_m)$ due to a collision with an atom having index i from $E(E')$, an index set for extra collisions for Me(Ma) within $[t_0, t_m^*]$ (where the fast collisions which don't count for Ma are indexed by E) or B, an index set for fast atoms which collide with both Me and Ma within $[t_0, t_m^*]$. Finally $\underline{F}_m(t_m^*)(\underline{F}'_m(t_m^*))$ denotes the change in $\underline{Z}_m(\tilde{\underline{Z}}'_m)$ due to the free motion within $[t_0, t_m^*]$. With

$$\begin{aligned}K_m^{(1)} &= |\underline{F}'(t_m^*) - \underline{F}(t_m^*)|, \\ K_m^{(2)} &= \sum_{i \in E'} |\underline{X}'_m(i)| + \sum_{i \in E} |\underline{X}_m(i)|, \\ K_m^{(3)} &= \sum_{i \in B} |\underline{X}'_m(i) - \underline{X}_m(i)|\end{aligned}$$

and

$$K_m^{(4)} = |\underline{Y}'_m(t_m^*)| + |\underline{Y}_m(t_m^*)|,$$

we obtain from (4.14) that

$$\{|\tilde{\underline{Z}}'_m(t_m^*)-\underline{Z}_m(t_m^*)|\geqq\varepsilon\}$$
$$\subset\bigcup_{j=1}^{4}\{K_m^{(j)}\geqq\varepsilon/5\}\cup\{|\underline{Z}'_m(t_0)-\underline{Z}_m(t_0)|\geqq\varepsilon/5\}\cup\{t_m^*\leqq t_0\},$$

and (4.8) holds if

$$\lim_{m\to 0}\bar{P}_m(G_n^m\cap\{t^*\leqq t_0+u\}\cap\{K_m^{(j)}\geqq\varepsilon/5\})=0,\qquad j=1,2,3,4,\tag{4.15}$$

since

$$\lim_{m\to 0}\bar{P}_m(G_n^m\cap\{|\tilde{\underline{Z}}'_m(t_0)-\underline{Z}_m(t_0)|\geqq\varepsilon/5\})=0$$

and

$$\lim_{m\to 0}\bar{P}_m(\{t_m^*\leqq t_0\})=0$$

by hypothesis (4.7)

We now establish (4.15). All the estimates we do are for $\bar{\omega}\in G_n^m$, $k\geqq 8n(1+r_0)$, $\varepsilon<n$ and m small enough so that $A<1/10$.

$j=1$. In view of (1.11) and (1.23)

$$K_m^{(1)}(\bar{\omega})\leqq\int_{t_0}^{t_m^*}\left|\begin{pmatrix}\underline{\tilde{W}}'_{m,s}(\bar{\omega})\times\underline{\tilde{V}}'_{m,s}(\bar{\omega})-\underline{W}_{m,s}(\bar{\omega})\times\underline{V}_{m,s}(\bar{\omega})\\ \mathbf{I}^{-1}\cdot(\underline{\tilde{W}}'_{m,s}(\bar{\omega})\times\mathbf{I}\cdot\underline{\tilde{W}}'_{m,s}(\bar{\omega}))-\mathbf{I}^{-1}\cdot(\underline{W}_{m,s}(\bar{\omega})\times\mathbf{I}\cdot\underline{W}_{m,s}(\bar{\omega}))\end{pmatrix}\right|ds$$
$$\leqq\int_{t_0}^{t_m^*}[|\underline{\tilde{W}}'\times\underline{\tilde{V}}'-\underline{\tilde{W}}'\times\underline{V}|+|\underline{\tilde{W}}'\times\underline{V}-\underline{W}\times\underline{V}|+|\mathbf{I}^{-1}(\underline{\tilde{W}}'\times\mathbf{I}\cdot\underline{\tilde{W}}'-\mathbf{W}\times\mathbf{I}\underline{\tilde{W}}')|$$
$$+|\mathbf{I}^{-1}\cdot(\underline{W}\times\mathbf{I}\cdot\underline{\tilde{W}}'-\underline{W}\times\mathbf{I}\cdot\underline{W})|]\,ds,\tag{4.16}$$

where $\underline{\tilde{W}}'=\underline{\tilde{W}}'_{m,s}(\bar{\omega})$, etc.

Using (4.12) and $|\underline{\tilde{W}}'|<n$, $|\underline{V}|<2n$, $|\underline{W}|<2n$ one obtains from (4.16) that

$$K_m^{(1)}(\bar{\omega})\leqq\int_{t_0}^{t_m^*}3\varepsilon n(1+(I_0^{-1}I^0)\,ds\leqq 3u\varepsilon n\{1+(I_0^{-1}I^0)\}<\varepsilon/5$$

for $u\leqq(16n(1+I_0^{-1}I^0))^{-1}$.

Thus

$$\lim_{m\to 0}\bar{P}_m(G_n^m\cap\{t_m^*\leqq t_0+u\}\cap\{K_m^{(1)}\geqq\varepsilon/5\})=0.$$

$j=2$. For the change $\delta\underline{Z}$ of $\underline{Z}$ due to a collision with a fast atom we have in view of (1.23)

$$|\delta\underline{Z}|\leqq 4m|\underline{v}_n|(1+r_0I_0^{-1}),\tag{4.17}$$

where $|\underline{V}^s(r)|<k\leqq|\underline{v}_n|$ has been used.

In view of (4.2) and (4.3) the rate for the occurrence of extra collisions including the "extra collisions" for Me is ($|\underline{v}_n|\geqq k$)

$$R_m^E(\underline{r},\underline{v},\tilde{\underline{Z}}',\underline{Z})=|R_m(\underline{r},\underline{v},\tilde{\underline{Z}}')-R_m(\underline{r},\underline{v},\underline{Z})|$$
$$=\lambda_m|\tilde{V}_n^{s'}(\underline{r})-V_n^s(\underline{r})|\,f_m(v),$$

since $\sup_{t<t_m^*} \zeta_{m,t} < k/4$,

using (3.9) with (3.4). By virtue of (3.13), (4.12) and (2.4)

$$|\tilde{V}_n^{s'}(\underline{r}) - V_n^s(\underline{r})| = |\underline{e}_n \cdot (\underline{\tilde{Z}}' - \underline{Z})| < \varepsilon(1+r_0) \tag{4.18}$$

for $t < t_m^*$.

As in [3] we introduce the Poisson field Y_m on the $(t, \underline{v})$ space determined by the rates $(|\underline{v}_n| > k)$

$$R_m^Y(\varepsilon, \underline{r}, \underline{v}) = m^{-1/2}\, \varepsilon(1+r_0) f_m(v) \tag{4.19}$$

which majorizes R_m^E.

Let $(\underline{v}^{(1)}, \ldots, \underline{v}^{(N)})$ represent the "extra collisions" during $[t_0, t_0+u]$ arising from Y_m. Then using (4.17) and the fact that the process Y_m, governed by the rates (4.19), may be obtained from the process of actual extra collisions by adding some more "collisions" (see the proof of Eq. (5.18) in [3]),

$$\begin{aligned} &\bar{P}_m(G_n^m \cap \{t_m^* \leqq t_0+u\} \cap \{K_m^{(2)} \geqq \varepsilon/5\}) \\ &\leqq P_m^Y\left(\sum_{i=1}^{N} 4m|\underline{v}_n^{(i)}|(1+r_0 I_0^{-1}) \geqq \varepsilon/5\right), \end{aligned} \tag{4.20}$$

where P_m^Y denotes the probability corresponding to Y_m. With $E_m^Y(\cdot)$ as the corresponding expectation we have using (4.19) and (2.6)

$$E_m^Y\left(\sum_{i=1}^{N} 4m|\underline{v}_n^{(i)}|(1+r_0 I_0^{-1})\right) \leqq 4m(1+r_0 I_0^{-1})\, u\, m^{-1}\, \varepsilon(1+r_0)\, \phi_1 \leqq \varepsilon/10$$

since $u \leqq (40(1+r_0)(1+r_0 I_0^{-1})\phi_1)^{-1}$.

Let $J_m = \sum_{i=1}^{N} |\underline{v}_n^{(i)}|$ and $\bar{J}_m = E_m^Y(J_m)$; then the r.h.s. of (4.20) can be estimated as follows:

$$P_m^Y(4m(1+r_0 I_0^{-1}) J_m \geqq \varepsilon/5) \leqq P_m^Y(J_m \geqq 2\bar{J}_m) = P_m^Y(J_m - \bar{J}_m \geqq \bar{J}_m).$$

(4.15) now follows using Cebyšev's inequality exactly as in [3].

$j=3$. By virtue of (3.13) and (3.14) and the definition of $\underline{\tilde{Z}}_m'$ we have that for $i \in B$ ($\underline{v}_n(i)$ = normal velocity of atom i)

$$\begin{aligned} |\underline{X}_m'(i) - \underline{X}_m(i)| &= \frac{2m}{A+1} |\underline{e}_n \cdot \mathscr{M}^{-1}(v_n(i) - \underline{\tilde{Z}}' \cdot \underline{e}_n - v_n(i) + \underline{Z} \cdot \underline{e}_n)| \\ &= \frac{2m}{A+1} |\underline{e}_n \cdot \mathscr{M}^{-1}(\underline{\tilde{Z}}' - \underline{Z}) \cdot \underline{e}_n| \\ &\leqq 2m\, \varepsilon(1+r_0)(1+r_0 I_0^{-1}), \end{aligned}$$

where we have used (4.12), (2.4), and (2.5). Hence

$$K_m^{(3)} \leqq 2m\, \varepsilon(1+r_0)(1+r_0 I_0^{-1})\, \tilde{N}_m'(u) \tag{4.21}$$

where $\tilde{N}_m'(u)$ is the number of collisions involving Ma within $[t_0, t_0+u]$.

Consider the Poisson process with rate (density) $2m^{-1}\phi_1$ and let $N_m^P(n)$ be the number of points in $[0,u]$ for this process. On G_m^n the "total rate" $\bar{\lambda}_m \leqq 2m^{-1}\phi_1$ since $|\tilde{\zeta}'|<k$. Therefore, using (4.21), we have that

$$\begin{aligned}
&\bar{P}_m(G_m^n \cap \{t_m^* \leqq t_0+u\} \cap \{K_m^{(3)} \geqq \varepsilon/5\}) \\
&\quad \leqq \mathrm{Prob}(2m\varepsilon(1+r_0)(1+r_0 I_0^{-1}) N_m^P(u) \geqq \varepsilon/5) \\
&\quad = \mathrm{Prob}(N_m^P(u) \geqq \{10m(1+r_0)(1+r_0 I_0^{-1})\}^{-1}) \\
&\quad \leqq \mathrm{Prob}(N_m^P(u) \geqq 2E(N_m^P(u))) \\
&\quad = \mathrm{Prob}(N_m^P(u) - E(N_m^P(u)) \geqq E(N_m^P(u))) \leqq E(N_m^P(u))^{-1}
\end{aligned} \tag{4.22}$$

for $u \leqq (40\phi_1(1+r_0)(1+r_0 I_0^{-1}))^{-1}$, by Cebyšev's inequality, yielding (4.15) for $j=3$.

$j=4$. To establish (4.15) for $j=4$ we estimate the total change in the velocity of a slow atom due to collisions with Me within $[t_0, t_m^*]$. This is the only estimate we cannot give for a general convex body. We assume that the surface of Me has bounded mean curvature. From this it follows that there exists a number $c>0$ such that for every point p on the surface S of Me there is a sphere of radius c tangent to S at p and entirely contained inside Me.

Consider a slow atom with speed $v(0)$ at $t=0$. Let

$$\bar{v} = \max(v(0), 3k)$$

and let Λ denote the volume of Me. In the following we show that the speed $v(t)$ of the slow atom during $[0, t_m^*]$ is bounded by

$$v(t) \leqq \tilde{v} = \bar{v} e^{K\Lambda}, \tag{4.23}$$

where $K>0$ is an appropriate constant.

We first consider a collision between Me and a slow atom with $|\underline{v}_t|>k$. With

$$\cos \Delta\Phi = \frac{\underline{v}^+ \cdot \underline{v}}{v^+ v}$$

we can estimate

$$\Delta v = v^+ - v \leqq |\underline{v}^+ - \underline{v}| \leqq 2v\Delta\Phi, \tag{4.24}$$

where we have used that by virtue of (1.16) and (1.17) $\left(\zeta < \frac{k}{4}\right) \underline{v}_t^+ = \underline{v}_t$, and $v_n \geqq v_n^+ \geqq -v_n - k \geqq -2k$ if $v_n>0$ and $0 \geqq v_n^+ \geqq -k$ if $v_n<0$.

Note that $\Delta\Phi$ is also the angle between the $\underline{v}^+$-plane and the $\underline{v}$-plane. We denote by $\Lambda(\Delta\Phi)$ the volume of the piece of Me which is in between the $\underline{v}^+$-plane and the $\underline{v}$-plane at the moment of the collision. As long as $v^+>k$, no piece of the surface of Me which is below (in $(-\underline{v}^+)$ direction) the $\underline{v}^+$-plane at the moment of collision can be involved in a future collision with this atom since $\sup_{t<t_m^*} \zeta \leqq k/4$ and each recollision increases the part of Me which is precluded from future recollisions. Suppose that in the ith collision between the atom (with velocity $\underline{v}_i$) and Me, $|\underline{v}_{i,t}|>k$; then

$$\Delta\Phi_i \leqq K' \Lambda(\Delta\Phi_i) \tag{4.25}$$

where $K'>0$ is an appropriate constant involving the radius c. Combining (4.25) and (4.24) yields ($K=2K'$)

$$v_i^+ - v_i = v_{i+1} - v_i \equiv \Delta v_i \leqq K v_i \Lambda(\Delta\Phi_i). \tag{4.26}$$

Suppose that the speeds of the slow atom in a sequence of successive collisions with Me during $[0, t_m^*]$ satisfy $v_i \geqq 2k$, $j+1 \leqq i \leqq j+N$, and that $v_j < 2k$ if $j>0$. Let $\tilde{v}_i = v_{j+i}$ and $\widetilde{\Delta\Phi}_i = \Delta\Phi_{j+i}$. Note that after the first collision of this sequence the $\underline{v}^+$-plane (which we think of as being attached to the atom) moves in direction of $\underline{v}_1^+$ with speed $v_1^+ > k$ through Me ($\zeta < k/4$, $t < t_m^*$) and enlarges the surface (and hence the piece of volume) of Me which is precluded from future collisions until the atomic collides again, adding $\Lambda(\widetilde{\Delta\Phi}_2)$ to this piece of volume, etc. Thus

$$\sum_{i=1}^{N} \Lambda(\widetilde{\Delta\Phi}_i) \leqq \Lambda. \tag{4.27}$$

(4.26) and (4.27) yield the upper bound (4.23) for the speed a slow atom can attain from collisions with Me within $[0, t_m^*]$: From (4.25) we obtain

$$\ln \tilde{v}_{i+1} - \ln \tilde{v}_i \leqq \frac{\Delta \tilde{v}_i}{\tilde{v}_i} \leqq K \Lambda(\widetilde{\Delta\Phi}_i)$$

and

$$\ln \tilde{v}_N^+ - \ln \tilde{v}_N \leqq \frac{\Delta \tilde{v}_N}{\tilde{v}_N} \leqq K \Lambda(\widetilde{\Delta\Phi}_N)$$

so that

$$\ln \frac{\tilde{v}_N^+}{\tilde{v}_1} = \sum_{i=1}^{N-1} (\ln \tilde{v}_{i+1} - \ln \tilde{v}_i) + \ln \tilde{v}_N^+ - \ln \tilde{v}_N \leqq K\Lambda,$$

i.e.,

$$v_{j+N}^+ = \tilde{v}_N^+ \leqq \tilde{v}_1 e^{K\Lambda} \leqq \bar{v} e^{K\Lambda}. \tag{4.28}$$

The last inequality in (4.28) follows from the fact that if $j=0$ $\tilde{v}_1 = v(0)$ and if $j \neq 0$ $|v_{j,n}^+| < k$ (since otherwise no further recollisions can occur). This establishes (4.23).

Next we estimate the change in $\underline{Z}$ due to one slow atom during $[t_0, t_m^*]$. Let $i=1, \ldots, N$ label the collisions of the slow atom with Me within $[t_0, t_m^*]$. In the ith collision the velocity of the atom changes by $\Delta \underline{v}_i$ and

$$\underline{V}_i^+ - \underline{V}_i = -m \Delta \underline{v}_i$$

so that

$$\left| \sum_{i=1}^{N} \underline{V}_i^+ - \underline{V}_i \right| = m \left| \sum_{i=1}^{N} \Delta \underline{v}_i \right|. \tag{4.29}$$

But

$$\underline{v}(t_m^*) - \underline{v}(t_0) = \sum_{i=1}^{N} \Delta \underline{v}_i + \Delta \underline{v}_{\text{free}} \tag{4.30}$$

where $\Delta \underline{v}_{\text{free}}$ denotes the change in $\underline{v}$ due to the free motion. By (1.10), (4.23) and the fact that on G_m^n during $[t_0, t_m^*]$ $|W| < 2n$,

$$|\Delta \underline{v}_{\text{free}}| \leqq \int_{t_0}^{t_m^*} dt\, |\underline{W} \times \underline{v}(t)| \leqq 2n u \tilde{v}$$

and we obtain from (4.29) using (4.30) and (4.23)

$$\left| \sum_{i=1}^{N} \underline{V}_i^+ - \underline{V}_i \right| \leqq m(2n u + 2)\tilde{v} = K_V m \tilde{v}. \tag{4.31}$$

To estimate the change in the angular velocity of Me due to collisions with the slow atom we use the conservation of angular momentum. Let $R(t)$ be the position vector of the atom, from the origin of $\hat{\Sigma}$, described in Σ and let

$$\underline{q}(t) = \underline{R}(t) - \underline{Q}(t) \tag{4.32}$$

be the position of the atom with respect to Σ. (We may assume that $Q(t_0) = 0$.) Let

$$\underline{l} = m\, \underline{q} \times \underline{v}. \tag{4.33}$$

Then with $\Delta \underline{l}_i$ = change of $\underline{l}$ in the i-th collision

$$\left| \sum_{i=1}^{N} \underline{W}_i^+ - \underline{W}_i \right| = \left| \sum_{i=1}^{N} \mathbf{I}^{-1} \cdot \Delta \underline{l}_i \right| \leqq I_0^{-1} \left| \sum_{i=1}^{N} \Delta \underline{l}_i \right| \tag{4.34}$$

and as before we estimate

$$|\sum_i \Delta \underline{l}_i| \leqq |\underline{l}(t_m^*)| + |\underline{l}(t_0)| + |\Delta \underline{l}_{\text{free}}|. \tag{4.35}$$

Using (4.32) and (4.23) and the fact that on G_m^n during $[t_0, t_m^*]$ $|V| < 2n$,

$$\begin{aligned} |\underline{l}(t_m^*)| &= m\, |\underline{R}(t_m^*) \times \underline{v}(t_m^*) - \underline{Q}(t_m^*) \times \underline{v}(t_m^*)| \\ &\leqq m\tilde{v}(r_0 + 2n u + 2n u) = m\tilde{v}(r_0 + 4n u), \end{aligned} \tag{4.36}$$

since

$$|\underline{R}(t_m^*) \times \underline{v}(t_m^*)| = |\underline{R}_N \times \underline{v}_N|.$$

Similarly

$$|\underline{l}(t_0)| = m\, |\underline{R}(t_0) \times \underline{v}(t_0)| \leqq m\tilde{v}(r_0 + 2n u). \tag{4.37}$$

To estimate $\Delta \underline{l}_{\text{free}}$ observe that in view of (1.6) $\left(\frac{d}{dt}\hat{\underline{l}} = 0\right)$

$$\begin{aligned} \left(\frac{d}{dt}\underline{l}\right)_{\text{free}} &= m \frac{d}{dt}(\underline{R} \times \underline{v} - \underline{Q} \times \underline{v}) \\ &= m(-\underline{W} \times (\underline{R} \times \underline{v}) - \underline{V} \times \underline{v} + \underline{W} \times (\underline{Q} \times \underline{v})) \end{aligned}$$

and thus

$$\begin{aligned} |\Delta \underline{l}_{\text{free}}| &\leqq m\tilde{v}u(2n(2n u + r_0) + 2n + 4n^2 u) \\ &= m\tilde{v}(2n u r_0 + 2n u + 8n^2 u^2). \end{aligned} \tag{4.38}$$

We thus obtain from (4.34) and (4.35)

$$\left|\sum_{i=1}^{N} \underline{W}_i^+ - \underline{W}_i\right| \leqq I_0^{-1} m\tilde{v}(2r_0 + 2nur_0 + 8nu + 8n^2u^2) = K_W m\tilde{v}. \tag{4.39}$$

Combining (4.31) with (4.39) we obtain

$$\left|\sum_{i=1}^{N} \underline{Z}_i^+ - \underline{Z}_i\right| \leqq m\tilde{v}(K_V + K_W) = m\tilde{v}K_Z. \tag{4.40}$$

To estimate $|\underline{Y}(t_m^*)|$ we have to sum the r.h.s. of (4.40) over the distinct slow atoms which hit Me during $[t_0, t_m^*]$. Let $\tilde{v}_i$, $i=1,\ldots,N_m$, be the values of v for the distinct slow atoms which first collide with Me during $[0,T]$ at times when $|\underline{Z}|<2n$ (so that $\zeta<k/4$). Then

$$|\underline{Y}(t_m^*)| \leqq mK_Z \sum_{i=1}^{N_m} \tilde{v}_i. \tag{4.41}$$

Note that in the $\tilde{Z}'$-process slow atoms don't recollide. Therefore the change in $\tilde{\underline{Z}}'$ due to a collision with a slow atom with velocity $\underline{v}$ is by (3.14) ($\tilde{\zeta}' \leqq k/8$)

$$|\tilde{\underline{Z}}'^+ - \tilde{\underline{Z}}'| \leqq m\,3k(1 + r_0 I_0^{-1}) = mK_Z'$$

and hence

$$|\underline{Y}'(t_m^*)| \leqq mK_z' N_m', \tag{4.42}$$

where N_m' denotes the number of slow atoms which collide with Ma during $[0,T]$ in which $|\tilde{\underline{Z}}'|<n$ (so that $\tilde{\zeta}' \leqq k/8$).

Since we are counting only collisions with slow atoms for which $\zeta<k$, $\tilde{\zeta}'<k$ we obtain from (3.1) that the rates for these collisions, both for Z_m and $\tilde{\underline{Z}}_m'$, are less than

$$R_s(\underline{v}) = m^{-1/2}\,2k f_m(v), \qquad (|\underline{v}_n|<k). \tag{4.43}$$

Just as before we obtain for (4.15), using (4.41) and (4.42),

$$\begin{aligned} &\bar{P}_m(G_n^m \cap \{t_m^* \leqq t_0 + u\} \cap \{K_m^{(4)} \geqq \varepsilon/5\}) \\ &\leqq \bar{P}_m\Big(m\Big(K_z \sum_{i=1}^{N_m} \tilde{v}_i + K_z' N_m'\Big) \geqq \varepsilon/5\Big) \\ &\leqq 5E^s\left(m\left(K_z \sum_{i=1}^{N_m^s} \tilde{v}(i) + K_z' N_m^s\right)\right)\Big/\varepsilon, \end{aligned} \tag{4.44}$$

where $E^s(\cdot)$ denotes the expectation for the process governed by the rates (4.43) and $\tilde{v}(i)$, $i=1,\ldots,N_m^s$, are the values of $\tilde{v}$ for the "collisions" in this process during $[0,T]$. Clearly $E^s(N_m^s) = 2m^{-1/2}kT$ and using (4.23)

$$\begin{aligned} E^s\left(\sum_{i=1}^{N_m^s} \tilde{v}(i)\right) &\leqq 2m^{-1/2}kT\left(\int_{-k}^{k}\int_{\mathbb{R}^2} v f_m(v)\,d\underline{v} + 3k\right) e^{K\Lambda} \\ &= 2m^{-1}kT\left(\int_{-k\sqrt{m}}^{k\sqrt{m}}\int_{\mathbb{R}^2} v f(v)\,d\underline{v} + m^{+1/2}3k\right) e^{K\Lambda}. \end{aligned}$$

Therefore taking $m\to 0$ in (4.44) yields (4.15) for $j=4$.

Appendix

The mechanical process $\underline{Z}_m$, $\underline{Q}_m$, θ_m has been defined only for those configurations $\omega \in \Omega$ and initial values $\underline{Z}_m(0)$, $\underline{Q}_m(0)$, $\theta_m(0)$ which in any finite time interval give rise to at most finitely many collisions none of which are tangential ($\underline{V}_n^s(\underline{r}) = \underline{v}_n$) or multiple collisions. Let B denote the set of configurations ω and initial values $\underline{Z}_m(0)$, $\underline{Q}_m(0)$, $\theta_m(0)$ which give rise to bad events: tangential, multiple or infinitely many collisions in a finite amount of time.

Proposition A.1. *Let λ denote the Lebesgue measure*[1] *on the state space Γ of $(\underline{Z}_{m,t}, \underline{Q}_{m,t}, \theta_{m,t})$ and $P_m \times \lambda$ the product measure on $\Omega \times \Gamma$. Then for any $m > 0$*

$$P_m \times \lambda(B) = 0. \quad \square$$

Proof. We may restrict ourselves to "finite" systems consisting of a molecule undergoing elastic collisions with finitely many atoms (see e.g. Appendix in [3]). Proposition A.1 is a consequence of

Proposition A.2. *For a finite system the set of bath configurations and initial values $\underline{Z}(0)$, $\underline{Q}(0)$, $\theta(0)$ which give rise to bad events has Lebesgue measure zero.* $\square$

Let B_N denote the set of bath configurations and initial values $\underline{Z}(0)$, $\underline{Q}(0)$, $\theta(0)$, in the finite system consisting of N atoms and the molecule, which give rise to bad events.
Let $\Lambda \subset \mathbb{R}^3$ be a finite cube and let $B_N(\Lambda, E)$ denote the subset of B_N in which $\underline{Q}(0) \in \Lambda$ and the energy $\left(MV^2 + \underline{W} \cdot \mathbf{I} \cdot \underline{W} + \sum_{i=1}^{N} m v_i^2\right) \Big/ 2$ of the system is less than or equal to E. Clearly

$$B_N = \bigcup_{\Lambda, E} B_N(\Lambda, E)$$

and Proposition A.2 will follow from

Proposition A.3. *For any $\Lambda, E, B_N(\Lambda, E)$ has Lebesgue measure zero.* $\square$

The proof of Proposition A.3 follows from a series of Lemmas. It suffices to consider the evolution of the system in the time interval $[0, 1]$. Fix Λ and E. Then there exists a cube $\bar{\Lambda} = \bar{\Lambda}(\Lambda, E)$ such that no atom which collides with the molecule can ever be outside of $\bar{\Lambda}$. We may assume that all N atoms interact with the molecule, since the Lebesgue measure of the set of configurations in $B_N(\Lambda, E)$ for which exactly $K < N$ of the atoms collide with the molecule is zero if $B_K(\Lambda, E)$ has Lebesgue measure zero. Let us consider a system S consisting of N atoms and the molecule in the box $\bar{\Lambda}$ with periodic boundary conditions and let $B_N(S)$ denote the set of initial values which give rise to bad events in this system. Then

$$B_N(\Lambda, E) \subset B_N(S)$$

since on $B_N(\Lambda, E)$ the motion of the molecule and the atoms in the finite system and system S are identical.

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[1] i.e., $d\lambda = d\underline{Z}\, d\underline{Q}\, d\theta$, where $d\theta$ is the unit Haar measure on $SO(3)$

Let τ denote the time of the first bad event. If this event involves infinitely many collisions in a finite amount of time, τ is the limit of the increasing sequence τ_k of collision times, $\tau = \lim_{k\to\infty} \tau_k$. Note that τ depends on the initial configuration. Until time τ the evolution of the system S is well defined. For $t<\tau$, let ϕ_t denote the mapping from the initial values of the phase space coordinates to the values at time t. Let λ_S be the Lebesgue measure on S. The evolution ϕ_t: $\{t<\tau\} \to \phi_t\{t<\tau\}$ preserves λ_S.

Lemma A.1. *Consider a system consisting of one atom and the molecule. Suppose that τ_k is an increasing sequence of times of collisions between the atom and the molecule with $\lim_{k\to\infty} \tau_k = \tau \leqq 1$. Then*

$$\lim_{k\to\infty} |\underline{v}_n(\tau_k) - \underline{V}_n^s(\underline{r}(\tau_k)| = 0,$$

where $V_n^s(\underline{r}(\tau_k))$ is the normal velocity of the surface point $\underline{r}(\tau_k)$ at which the collision at time τ_k takes place. □

Proof. We note (see Eq. (1.22)) that in a collision

$$|\underline{v}_n - \underline{V}_n^s(\underline{r})| = |\underline{v}_n^+ - \underline{V}_n^{s+}(\underline{r})|,$$

i.e. a collision does not change the relative normal velocity. If $|\underline{v}_n - \underline{V}_n^s(r)| > \varepsilon > 0$ in a collision, a time $\delta(\varepsilon) > 0$ must elapse before the next collision.

Lemma A.2. *The Lebesgue measure of the set $B_1(\Lambda, E)$ is zero for any Λ, E.* □

Proof. By Lemma A.1 we only have to consider tangential collisions. Let $\tilde{\tau} \geqq 0$ be the time of the first tangential collision.

For $0 \leqq t \leqq \tilde{\tau}$, let $\underline{d}(t)$ denote the vector from the atom to the nearest surface point $\underline{r}(t)$ of Me. By $\underline{v}_n(t)(\underline{V}_n^s(\underline{r}(t)))$ we denote the projection of $\underline{v}(t)(\underline{V}^s(\underline{r}(t)))$ on $\underline{d}(t)$. We split the time interval $[0, 1]$ into p left open intervals Δ_j, $j = 0, \ldots, p-1$, of length $1/p$. Let $\Gamma_j \subset B_1(\Lambda, E)$ denote the set of initial values $\underline{q}_0, \underline{v}_0, \underline{Q}_0, \underline{Z}_0, \theta_0$ which lead to a first tangential collision in Δ_j. The event that a tangential collision occurs is then included in $\bigcup_{j=0}^{p-1} \Gamma_j$ and hence it is enough to show that

$$\lambda_S(\Gamma_j) = o(1/p). \tag{A.1}$$

Since

$$\phi_{j/p}(\Gamma_j) \subset \Gamma_0$$

(A.1) follows by conservation of Lebesgue measure from

$$\lambda_S(\Gamma_0) = o(1/p). \tag{A.2}$$

To obtain this we note that $\underline{d}(t)$ is a piecewise differentiable function with (where the derivative exists)

$$\sup_{0 \leqq t \leqq \tilde{\tau}} |\underline{d}'(t)| \leqq C_1 < \infty, \tag{A.3}$$

where C_1 is an appropriate constant, and similarly

$$\sup_{0 \leqq t \leqq \tilde{\tau}} |\underline{v}(t) - \underline{V}^s(\underline{r}(t))|' | \leqq C_2 < \infty \tag{A.4}$$

(Note that in a collision $\underline{v}_n(t) - \underline{V}_n^s(\underline{r}(t))$ just reverses direction (Eq. (1.22.))

Thus on Γ_0

$$0 = \underline{d}(\tilde{\tau}) = \underline{d}(0) + \int_0^{\tilde{\tau}} \underline{d}'(t)\, dt$$

so that

$$|\underline{d}(0)| \leqq C_1/p. \tag{A.5}$$

Similarly,

$$0 = |\underline{v}_n(\tilde{\tau}) - \underline{V}_n^s(\underline{r}(\tilde{\tau}))| = |\underline{v}_n(0) - \underline{V}_n^s(\underline{r}(0))| + \int_0^{\tau} |\underline{v}_n(t) - \underline{V}_n^s(\underline{r}(t))|'\, dt$$

so that

$$|\underline{v}_n(0) - \underline{V}_n^s(\underline{r}(0))| \leqq C_2/p. \tag{A.6}$$

Since the phase space of the system is bounded (A.2) follows from (A.5) and (A.6).

Similarly one obtains (using just (A.3) for several atoms)

Lemma A.3. *For any Λ, E, the set $M \subset B_N(\Lambda, E)$ of initial values leading to a multiple collision has Lebesgue measure zero.* □

Proposition A.3 follows now by induction. Let $\hat{\tau} = \min(\tau, 1)$. The evolution is well defined up to time $\hat{\tau}$. We want to show that $\hat{\tau} = 1$ almost surely. We take as the induction hypothesis that for a system with $N-1$ atoms $\hat{\tau} = 1$ a.s. By Lemma A.2 we have that for $N = 1$, $\hat{\tau} = 1$ a.s.

For N atoms we have either (i) $\hat{\tau} = 1$ a.s., or (ii) all atoms are on the molecule at time $\hat{\tau}$. Otherwise there exists an $\varepsilon > 0$ such that during the interval $[\hat{\tau} - \varepsilon, \hat{\tau}]$ at most $N-1$ atoms collide with the molecule. Denote this event by $B(\varepsilon)$. For t_k an enumeration of the rationals, let B_k denote the event that $\hat{\tau} > t_k$ and at most $N-1$ atoms collide with the molecule during $[t_k, \hat{\tau}]$. Clearly $B(\varepsilon) \subset \bigcup_k B_k$ and B_k (and hence $B(\varepsilon)$) is by the induction hypothesis and the invariance of Lebesgue measure incompatible almost surely with $\hat{\tau} < 1$. But (ii) is excluded almost surely by Lemma A.3.

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